

available at www.sciencedirect.comjournal homepage: www.elsevier.com/locate/ijggc

Environmental impacts of absorption-based CO₂ capture unit for post-combustion treatment of flue gas from coal-fired power plant

Bhurisa Thitakamol, Amornvadee Veawab^{*}, Adisorn Aroonwilas

Faculty of Engineering, University of Regina, Regina, Saskatchewan, Canada S4S 0A2

ARTICLE INFO

Article history:

Received 10 August 2006

Received in revised form

23 March 2007

Accepted 23 March 2007

Published on line 7 May 2007

Keywords:

Environmental impact

CO₂ capture

Amine treating plant

Coal-fired power plant

Waste disposal

Air pollution

ABSTRACT

This study assesses potential environmental impacts of the absorption-based carbon dioxide (CO₂) capture unit that is integrated to coal-fired power plant for post-combustion treatment of flue gas. The assessment was performed by identifying potential pollutants and their sources as well as amounts of emissions from the CO₂ capture unit and also by reviewing toxicology, potential implications to human health and the environment, as well as the environmental laws and regulations associated with such pollutants. The assessment shows that, while offering a significant environmental benefit through a reduction of greenhouse gas emissions, the installation of CO₂ capture units for post-combustion treatment might induce unintentional and potential burdens to human health and the environment through four emission pathways, including treated gas, process wastes, fugitive emissions, and accidental releases. Such burdens nevertheless can be predetermined and properly mitigated through a well-established environmental management program and mitigation measures. Recommendations to minimize these impacts are provided in this paper.

© 2007 Elsevier Ltd. All rights reserved.

1. Introduction

Coal-fired power plants generate electricity by combusting coal to produce high pressure steam, which drives a series of turbines or generators. The coal combustion produces flue gas containing a number of air pollutants currently being regulated or expected to be regulated in the near future under various environmental laws and regulations. These pollutants include hazardous pollutants, such as mercury (Hg), and also criteria pollutants such as particulate matter (PM), sulphur oxides (SO_x), and nitrogen dioxide (NO₂). The coal-fired power plants also produce and release carbon dioxide (CO₂) to the atmosphere, a major greenhouse gas contributing to global climate change. The CO₂ emission is of great concern due to its large quantity and implications for the environment. It is

predicted that coal combustion could contribute approximately 41% of the total world CO₂ emissions (43,676 million metric tonnes of CO₂) in 2030. The coal combustions from the United States and Canada are predicted to contribute about 17.8 and 1.4%, respectively, of the world CO₂ emissions from coal in 2030 (Energy Information Administration, 2006).

To enforce the reduction of global greenhouse gas emissions, the Kyoto Protocol was established in December 1997 at the United Nations Framework Convention on Climate Change with a global reduction target of at least 5% below 1990 levels by the period of 2008–2012. The Protocol is currently ratified by 162 countries, including Canada, whose reduction target is 6% (Energy Information Administration, 2006, 2005). One of the reduction strategies to help Canada

^{*} Corresponding author. Tel.: +1 306 5855665; fax: +1 306 5854855.

E-mail address: veawab@uregina.ca (A. Veawab).

1750-5836/\$ – see front matter © 2007 Elsevier Ltd. All rights reserved.

doi:10.1016/S1750-5836(07)00042-4

VISIT...

LANZAROTE
Caliente.COM

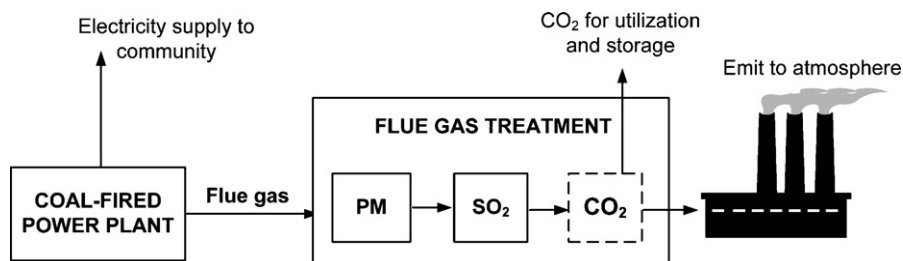


Fig. 1 – Schematic diagram of the integration of a CO₂ capture unit to a coal-fired power plant.

and other nations achieve its protocol target is to capture CO₂ from combustion flue gas streams generated by coal-fired power plants. This strategy also ensures the continuation of fossil fuel utilization in an environmentally sustainable manner. The CO₂ capture unit can be integrated to the power plant as a flue gas post-treatment unit with the arrangement shown in Fig. 1 to treat the flue gas after the removal of PM and SO₂ in order to prevent plugging and fouling, and to minimize degradation of CO₂ capture solvents. Although CO₂ capture can be technically implemented by a number of gas separation methods, gas absorption into liquid solvent is the most attractive because of its maturity in gas treating services. An example of an existing power plant with an amine absorption-based CO₂ capture unit is the Warrior Run power station in Cumberland, USA. This station has a capacity of 150 tonnes/day of CO₂ captured (Davison et al., 2001).

The integration of CO₂ capture units to coal-fired power plants is not a common practice. The power plants will require a proper project planning and decision making that should include the integrated consideration of technology, economics, environment, societal implications, and other factors in order to ultimately arrive at actions that are more environmentally compatible. Such actions should attain the widest range of beneficial uses of the resources without degrading the environment, risk to health or safety, and/or other undesirable or unintended consequences. It is therefore important and worthwhile to examine how CO₂ capture units would affect power plants from an environmental perspective. This work provides environmental inventory, implements environmental impact assessment, and addresses any potential burdens to humans and the environment resulting from the installation of CO₂ capture units using chemical absorption in coal-fired power plants as a post-combustion treatment unit. The present work also suggests appropriate mitigation measures, which could be applied to reduce the adverse impacts within reasonable environmental and economic constraints.

2. Environmental assessment methodology

The environmental assessment was implemented using a systematic procedure, as shown in Fig. 2. The procedure involved four sequential steps (i.e., capture-process audit, material-toxicology audit, environmental-law audit, and determination of emission distribution). The capture-process audit began with a review of process operation, followed by identifying process fluids and materials together with their

points of input and discharge or emission from the capture process. The process fluids and materials considered in the assessment are flue gas and materials such as absorption solvents, chemical additives, solid sorbent for solution filtration, makeup water, and waste products from process

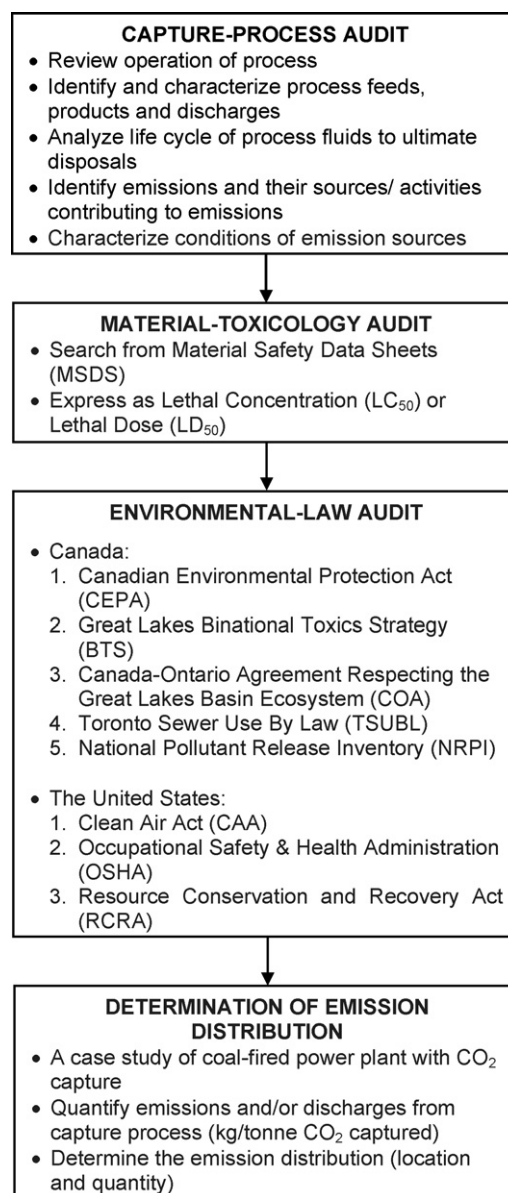


Fig. 2 – Methodology for environmental assessment of a CO₂ capture unit.

operation. The audit of process materials focused on how the use of such materials contributes to their emission or discharge to the environment and how the disposal of these materials can be handled. This essentially covered the life cycle of the fluids and materials, starting from their inputs to their ultimate disposals or discharges. The waste products were characterized by how they are generated, disposed of, and also whether volatile-type wastes can contribute to any emissions to the atmosphere. Each point of discharge was examined by considering strength and variability (i.e., flow rate, temperature, and concentration) of various pollutants within the process. Emission estimation was performed using relevant engineering thermodynamic and design equations as well as emission factors obtained from actual measurements for similar emission sources. It should be noted that this work excluded the consideration of environmental, geographic, or atmospheric conditions, which affect the distribution and dispersion of pollutants from the sources of discharge into the air.

The toxicology audit was done by examining the toxicological information of all materials involved, which was obtained from the Material Safety Data Sheet (MSDS). The toxicology data in this work are represented in terms of lethal dose-50 (LD_{50}) and lethal concentration-50 (LC_{50}). The tested animals for LD_{50} and LC_{50} were often small animals, such as rat and rabbits, but sometimes even humans were tested. These animals were exposed to the tested substances through inhalation (IHL), oral (ORL), or skin.

The environmental-law audit was conducted by reviewing the current environmental regulations in North America, including Canada and the United States. The Canadian regulations include the Canadian Environmental Protection Act (CEPA) (Canada Gazette Part III, 1999), the Toronto Sewer Use By Law (TSUBL) (Toronto Municipal Code, 2003), the National Pollutant Release Inventory (NRPI) (Canada Gazette

Part I, 2001), Great Lakes Binational Toxics Strategy (1997), and the Canada-Ontario Agreement Respecting the Great Lakes Basin Ecosystem (The Government of Canada and Ontario, 2002). The United States regulations under the Clean Air Act (CAA) included the New Source Performance Standards (NSPS) and the National Emission Standards for Hazardous Air Pollutants (NESHAP) (Clean Air Act). The toxic and hazardous substances are under the control of the Occupational Safety & Health Administration (OSHA) for safety in the workplace. These substances are listed in the Resource Conservation and Recovery Act (RCRA).

Finally, an overall emission distribution within the CO_2 capture unit was determined to provide an overview of where and how much the potential toxic emissions are discharged. The emission distribution was based on a case study of a coal-fired power plant integrated with a CO_2 capture unit. All emissions were quantified and presented in terms of mass of discharge per mass of CO_2 captured (i.e., kg/tonne CO_2).

3. Characterization of CO_2 absorption process

3.1. Process description

Fig. 3 illustrates a typical configuration of the CO_2 absorption process using regenerable liquid solvent. The process consists of two major sections, an absorption section where CO_2 in the flue gas is absorbed into the liquid solvent and a regeneration section where the absorbed CO_2 is stripped out by means of heat. In the absorption section, the gas stream containing CO_2 is passed upward through the absorber, countercurrent to the solvent entering the absorber at the top. Under proper conditions, CO_2 is transferred from the gas stream to the liquid solvent, resulting in a treated gas with low CO_2 content passing out of the absorber top and a CO_2 -rich solvent leaving

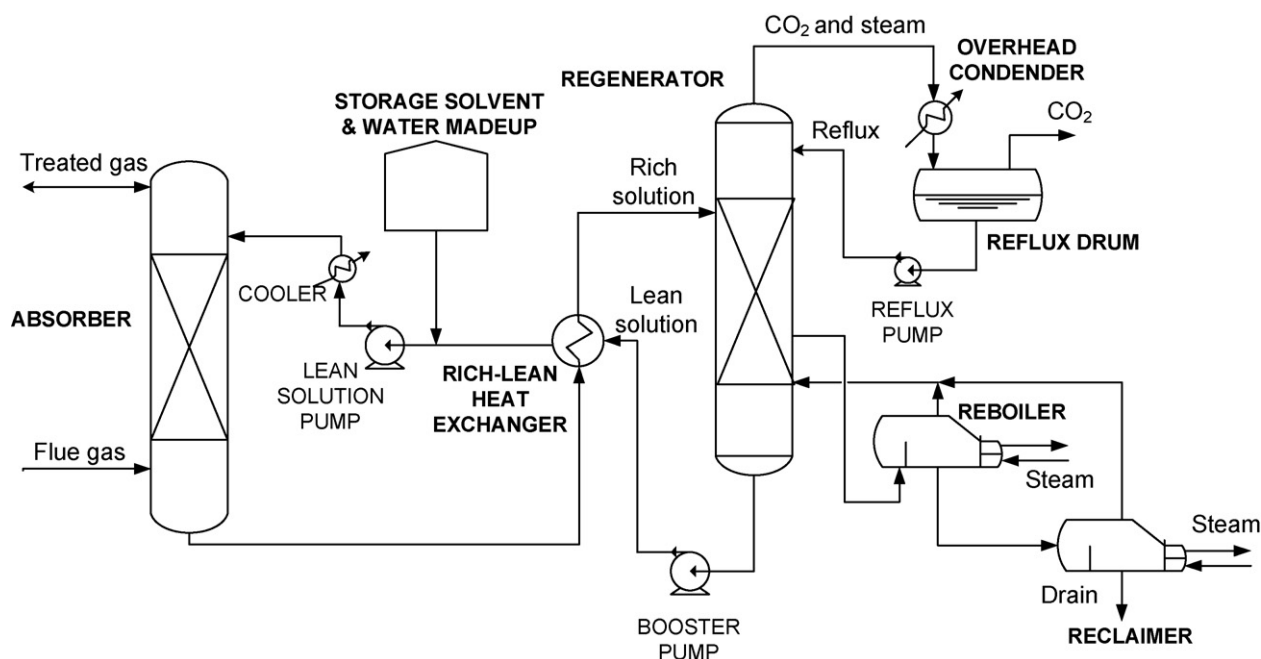


Fig. 3 – Schematic diagram of the typical absorption-based CO_2 capture unit.

the absorber at the bottom. The rich solvent is then heated in a rich-lean heat-exchanger, and enters the regenerator at some point near the top. The CO₂-rich solvent is heated to boiling in the regeneration section by a hot steam reboiler located at the bottom of the regenerator, and the captured CO₂ is released from the solvent. Finally, the CO₂-lean solvent is pumped from the regenerator through the rich-lean heat-exchanger and a cooler before re-introducing to the absorber.

One may recognize that the chemical solvents for CO₂ capture are subjected to the solvent degradation problem, which causes an accumulation of non-regenerable and inactive products in the process. A reclaiming attached to the hot steam reboiler is used periodically to remove such degradation products, particularly when the level of these products exceeds certain amounts (e.g., 1.2 wt% heat-stable salt anion of solution (CCR Technologies Inc.) or 10 wt% degradation products of active alkanolamine) (DuPart et al., 1993). The inline filtration is also used in parallel to remove some of the degradation products. Storage tanks for water and amine are in use for making up the solvent concentration due to the degradation and solvent loss, thereby maintaining the desired CO₂ capture efficiency of the process.

3.2. Process service

Process service comprises four categories of fluids entering and leaving the process (i.e., (i) flue gas from combustion process or post-treatment units, (ii) process utilities such as steam and cooling water, (iii) process solution for CO₂ capture, and (iv) solution makeup). The flue gas and process utilities enter and leave the process on a continuous basis, whereas the process solution is circulated continuously within the process with periodic make-up from storage tanks. Since the process utilities do not contribute directly to the additional emissions of pollutants, they are not included in the following discussions.

3.2.1. Flue gas

The flue gas generated from coal combustion contains a large number of substances, which can be classified into five categories (i.e., particulate matter (PM), gaseous component, organic compound, dioxin and furan, and trace metal or element). The quantity of each substance in the flue gas is dependent upon the type of coal and the design of the coal combustor. It should be noted that the emissions given in Table 1 are the emissions after the removal of PM and/or SO_x, except for those from anthracite combustion, which were taken before post-treatments.

Four types of coal, namely anthracite, bituminous, sub-bituminous, and lignite are included in the assessment in this work. As shown in Table 2, the anthracite and lignite are mostly found in Europe and Asia, while the bituminous and sub-bituminous are predominant in North America and Asia (Energy Information Administration, 2003). The flue gas from the anthracite combustion is considered cleaner than the flue gas from other coal types due to the smaller contents of toxic substances such as hydrogen chloride (HCl), hydrogen fluoride (HF), and organic compounds. The amounts of gaseous components such as carbon monoxide (CO), CO₂, oxides of sulphur (SO_x), and oxides of nitrogen (NO_x) can vary with the

supply rate of oxygen (O₂) to the combustion process and also with coal compositions (contents of carbon, sulphur, nitrogen, etc.).

Type or design of coal combustor plays a key role in the quality of flue gas produced. Generally, combustors are categorized into stoker-fired systems (i.e., underfeed stoker, overfeed stokers, and spreader stoker), fluidized bed combustors (FBC), pulverized coal-fired (PC) boilers, hand-fired units, and cyclone furnaces. The hand-fired units are widely used in industries that employ anthracite, and the stoker-fired systems are generally used in boilers that utilize bituminous/sub-bituminous (U.S. Environmental Protection Agency, 1995). Different types of combustor are known to produce different amounts of gaseous components and particulate matters. For instance, in the case of anthracite, as shown in Table 3, PC results in the highest amount of NO_x, whereas FBC produces the least.

3.2.2. Process solution

3.2.2.1. Absorption solvent. At present, there are a number of absorption solvents commercially available for CO₂ capture. They are classified into two categories, chemical and physical solvents. The chemical solvents are commonly used for treating gas streams with low- and moderate-CO₂ partial pressure, while the physical solvent is suitable for high-pressure gas streams. The typical chemical solvents are alkanolamines, which are commonly used in the form of aqueous solutions. These chemical solvents include monoethanolamine (MEA), diethanolamine (DEA), N-methyldiethanolamine (MDEA), diglycolamine (DGA), diisopropanolamine (DIPA), and 2-amino-2-methyl-1-propanol (AMP) (see Table 4). Mixtures of these single alkanolamines, known as blended amines, are also gaining a great deal of interest from the practitioners due to their process advantages over the single alkanolamines. Most formulations of the blended amines are tertiary amine-based, which are designed to be used for specific CO₂ capture targets and purposes. The tertiary MDEA is gaining recognition as the key component of the blended amines because of its low energy requirements and high CO₂ absorption capacity. An addition of primary amine MEA or secondary amine DEA into the MDEA solution helps enhance rate of capturing CO₂, while maintaining the advantages of MDEA.

Table 4 also includes some of the physical solvents in the list. These physical solvents are commonly used for high-pressure gas streams. They require less energy for solvent regeneration than the chemical solvents. Examples of physical solvents are propylene carbonate (PC), Selexol, methanol, and *n*-methyl-2-pyrrolidone (NMP). It is commonly known that use of physical solvent alone is ineffective for low-pressure gas streams. However, mixing of the chemical and physical solvents could provide some benefits for CO₂ capture under low-pressure conditions. For instance, blends of physical and chemical solvents such as sulphinol-D (sulpholane and DIPA) and sulphinol-M (sulpholane and MDEA) are found effective for the removal of CO₂ and sulphur compounds (e.g., SO₂) from gas streams (Gupta et al., 2003). Sulpholane works as a large storage species for captured CO₂ while both DIPA and MDEA (chemical solvents) work as the reactive species for capture activities. These mixed solvents also help reduce the corrosion rate and foaming problems.

Table 1 – Emissions from combustion of various types of coal

Substance (U.S. Environmental Protection Agency, 1995)	Emission (kg/Mg) (U.S. Environmental Protection Agency, 1995)			Toxicity ^a			Impact	Laws and regulation ^b	
	Anthracite coal	Bituminous-sub-bituminous coal	Lignite coal	LD ₅₀ -ORL (mg/kg)		Other toxicity		Canada	U.S.
				Mouse (MUS)	Rat (RAT)				
Particulate matter (PM) ^{c,d}									
Filterable	5, 0.4A	4.5–33, A–5A	0.005A–0.04A	–	–	–	- Damage respiratory system	1	1
Filterable PM-10 (diameter < 10 μm)	–	2.5–6.6, 0.13A–1.3A	–	–	–	–			
GAS ^{e,f,g}									
Carbon dioxide	2840	2405–3125	36.3C	–	–	2000 ppm (IHL-HMN LDLO)	- Asphyxiant	–	2
Carbon monoxide	0.3	0.25–137.5	0.075–0.125	–	–	–	- Toxic if inhaled	5	2
Hydrogen chloride	–	0.6	0.6	–	–	1300 ppm/30 m (IHL-HMN LCLO)	- Irritation and burns - May be fatal if inhaled	5	2–3
Hydrogen fluoride	–	0.075	0.075	–	1276	–	- Very toxic - Maybe fatal if inhaled and swallowed	5	1–3
Methane	No data	0.005–2.5	–	–	–	–	- Asphyxiant	–	–
Nitrogen oxides	0.9–9	2.5–16.5	1.8–7.5	–	–	NO ₂ : 200 ppm/1 h (IHL-HMN LCLO) NO: 1068 mg/m3/4 h (IHL-RAT LC50)	- NO ₂ : very toxic and fatal if inhaled; NO: may be fatal if inhaled; N ₂ O: asphyxiant at high concentration	1, 5	1–3
Sulphur oxides	1.45, 19.5S	15.5S–19S	5S–15S	–	–	SO ₂ :1000 ppm/10 m (IHL-HMN LCLO)	- SO ₂ : toxic; SO ₃ : may be fatal if contacted skin, inhaled and swallowed	1, 5	1–2
Organic compound									
Polynuclear aromatic hydrocarbon (PAH) ^h									
Acenaphthene	–	2.55E–07	2.55E–07	–	1700	–	- Eye, skin and respiratory irritation - May be harmful if inhaled and swallowed	–	–
Acenaphthylene	–	1.25E–07	1.25E–07	1760	–	–	- Eye, skin and respiratory irritation - May be harmful if contacted skin, inhaled and swallowed	–	–

Anthracene	–	1.05E–07	1.05E–07	4900	–	–	- Eye, skin and respiratory irritation - Carcinogen	1–3, 5	–
Benzo(a)anthracene	–	4.0E–08	4.0E–08	–	–	–	- Eye, skin and respiratory irritation - Carcinogen	1–3, 5	3
Benzo(a)pyrene	–	1.9E–08	1.9E–08	–	–	–	- Eye, skin and respiratory irritation - May be harmful if contacted skin, inhaled and swallowed - Carcinogen	1–2, 5	2–3
Benzo(b)fluoranthene	–	0.55E–07	0.55E–07	–	–	–	- Carcinogen - Very harmful to aquatic organisms	1, 3, 5	3
Benzo(j)fluoranthene	–	0.55E–07	0.55E–07	–	–	–	–	1, 5	–
Benzo(k)fluoranthene	–	0.55E–07	0.55E–07	–	–	–	- Eye, skin and respiratory irritation - May be harmful if contacted skin, inhaled and swallowed - Carcinogen	1, 5	–
Benzo(g,h,i)perylene	–	1.35E–08	1.35E–08	–	–	–	- Skin irritation	1–3, 5	–
Biphenyl	0.0125	8.5E–07	8.5E–07	1900	2140	–	- Eye, skin and respiratory irritation	5	1
Chrysene	–	0.5E–07	0.5E–07	–	–	–	- Eye, skin and respiratory irritation - Carcinogen	1, 5	2–3
Fluoranthene	–	3.55E–07	3.55E–07	–	2000	–	- Eye irritation - May be harmful if contacted skin and swallowed	1, 5	3
Fluorene	–	4.55E–07	4.55E–07	–	–	–	- Eye, skin and respiratory irritation - Harmful if inhaled and swallowed - Carcinogen	–	–
Indeno (123-cd)pyrene	–	3.05E–08	3.05E–08	–	–	–	–	1, 5	3
5-Methylchrysene	–	1.1E–08	1.1E–08	–	–	–	–	–	–
Naphthalene	0.065	0.65E–05	0.65E–05	316	490	–	- Eye, skin and respiratory irritation - Carcinogen	1, 5	1–3
Phenanthrene	3.4E–03	1.35E–06	1.35E–06	700	1800	–	- Eye, skin and respiratory irritation - Harmful dust - Carcinogen	1–3, 5	2

Table 1 (Continued)									
Substance (U.S. Environmental Protection Agency, 1995)	Emission (kg/Mg) (U.S. Environmental Protection Agency, 1995)			Toxicity ^a			Impact	Laws and regulation ^b	
	Anthracite coal	Bituminous-sub-bituminous coal	Lignite coal	LD ₅₀ -ORL (mg/kg)		Other toxicity		Canada	U.S.
				Mouse (MUS)	Rat (RAT)				
Pyrene	–	1.65E–07	1.65E–07	800	2700	–	- Eye, skin and respiratory irritation - May be fatal if inhaled - May be harmful if swallowed - Carcinogen	1, 5	–
Volatile organic compound (VOC) ^h									
Acetaldehyde	–	2.85E–04	2.85E–04	900	661	–	Eye (severe), skin and respiratory irritation - May be harmful if inhaled - Carcinogen	1, 5	1–3
Acetophenone	–	7.5E–06	7.5E–06	1250	815	–	- Eye (severe) and respiratory irritation - May be harmful if inhaled	5	1, 3
Acrolein	–	1.45E–04	1.45E–04	13.9	–	–	- Severe eye, skin and respiratory irritation and possible burns - May be fatal if contacted skin and swallowed	1, 5	1–3
Benzene	–	6.5E–04	6.5E–04	4700	930	–	- Eye, skin and respiratory irritation - May be harmful if contacted skin - Carcinogen	1, 4–5	1–3
Benzyl chloride	–	3.5E–04	3.5E–04	–	1231	–	- Harmful if inhaled - Carcinogen	5	1–3
Bis(2-ethylhexyl)phthalate (DEHP)	–	3.65E–05	3.65E–05	29,500	30,000	–	- Eye, skin and respiratory irritation - Carcinogen	1, 4–5	1, 3
Bromoform	–	1.95E–05	1.95E–05	1072	933	–	- Eye, skin and respiratory irritation - Carcinogen	–	1–3
Carbon disulphide	–	6.5E–05	6.5E–05	2780	1200	–	- Eye (severe) and skin irritation	5	1–3

2-Chloroacetophenone	–	3.5E–06	3.5E–06	139	50	–	- Eye, skin and respiratory irritation - Harmful if swallowed	–	1–2
Chlorobenzene	–	1.1E–05	1.1E–05	2300	1100	–	- Eye, skin and respiratory irritation - Carcinogen	5	1–3
Chloroform	–	2.95E–05	2.95E–05	36	695	–	- Eye (moderate) and skin (mild) irritation - Carcinogen	4–5	1–3
Cumene	–	2.65E–06	2.65E–06	12,750	1400	–	- Eye, skin and respiratory irritation - May be harmful if swallowed	5	1–3
Cyanide	–	1.25E–03	1.25E–03	3.7		–	- Very toxic if inhaled	5	2–3
2,4-Dinitrotoluene	–	1.4E–07	1.4E–07		268	–	- Highly toxic - Carcinogen	5	1, 3
Dimethyl sulphate	–	2.4E–05	2.4E–05	140	205	–	- Eye and skin burns -Harmful if swallowed - May be fatal if inhaled - Carcinogen	5	1–3
Ethyl benzene	–	4.7E–05	4.7E–05	–	3500	–	- Eye, skin and respiratory irritation - Carcinogen	4–5	1–2
Ethyl chloride	–	2.1E–05	2.1E–05	–	–	15,200 mg/m ³ / 2 h (IHL-RAT LC50)	- Harmful to environment - Carcinogen	5	1–2
Ethylene dichloride	–	2.0E–05	2.0E–05	413	500	–	- Eye, skin and respiratory irritation - Carcinogen	1, 5	1–3
Ethylene dibromide	–	6.0E–07	6.0E–07	–	108	–	- Severe eye and skin irritation - Harmful if contacted skin and swallowed - Carcinogen	–	1–3
Formaldehyde	–	1.2E–04	1.2E–04	42		–	- Eye and skin burns - Respiratory irritation - May be fatal if swallowed - Carcinogen	5	1–3
Hexane	–	3.35E–05	3.35E–05	–	25,000	–	- Eye (mild), skin and respiratory irritation	5	1–2

Table 1 (Continued)

Substance (U.S. Environmental Protection Agency, 1995)	Emission (kg/Mg) (U.S. Environmental Protection Agency, 1995)			Toxicity ^a			Impact	Laws and regulation ^b	
	Anthracite coal	Bituminous-sub-bituminous coal	Lignite coal	LD ₅₀ -ORL (mg/kg)		Other toxicity		Canada	U.S.
				Mouse (MUS)	Rat (RAT)				
Isophorone	–	2.9E–04	2.9E–04	2690	1870	–	- Eye (severe) and skin irritation - May be harmful if contacted skin - Carcinogen	–	1–2
Methyl bromide	–	8.0E–05	8.0E–05	–	214	–	- May be fatal if contacted skin, inhaled and ingested - Carcinogen	1, 5	1–3
Methyl chloride	–	2.65E–04	2.65E–04	–	1800	–	- Toxic if inhaled - Carcinogen	5	1–3
Methyl ethyl ketone	–	1.95E–04	1.95E–04	3000	2737	–	- Eye and respiratory irritation	5	2–3
Methyl hydrazine	–	8.5E–05	8.5E–05	29	32	–	- Eye irritation - May be fatal if contacted skin, inhaled and swallowed - Carcinogen	–	1–3
Methyl methacrylate	–	1.0E–05	1.0E–05	3625	7872	–	- Eye, skin and respiratory irritation	5	1–3
Methyl <i>tert</i> -butyl ether	–	1.75E–05	1.75E–05	–	4000	–	- Eye, skin and respiratory irritation - Carcinogen	5	1
Methylene chloride	–	1.45E–04	1.45E–04	–	–	52,000 g/m ³ (IHL-RAT LC50)	- Eye (severe) and respiratory irritation - Carcinogen	1, 4–5	1–3
Phenol	–	8.0E–06	8.0E–06	270	317	–	- Severe eye burn - May be fatal if contacted skin - Severe respiratory irritation	5	1–3
Propionaldehyde	–	1.9E–04	1.9E–04	–	1410	–	- Eye (severe), skin (mild) and respiratory irritation - May be harmful if swallowed	5	1
Tetrachloroethylene	–	2.15E–05	2.15E–05	6400	2629	–	- Eye, skin (severe) and respiratory irritation - Carcinogen	1, 4–5	1–3
Toluene	–	1.2E–04	1.2E–04	–	636	–	- Eye, skin and respiratory irritation	4–5	1–3

Styrene	–	1.25E–05	1.25E–05	316	2650	–	- Eye irritation - Carcinogen	5	1–2
Vinyl acetate	–	3.8E–06	3.8E–06	1600	2900	–	- Eye (severe) and skin (mild) irritation - Harmful if inhaled - Carcinogen	5	1
Xylenes	–	1.85E–05	1.85E–05	2119	4300	–	- May be harmful if contacted skin - Respiratory irritation	4–5	1–3
Various organic compound 1,1,1-Trichloroethane ^h	–	1.0E–05	1.0E–05	6000	9600	–	- Eye (mild) and skin irritation	1	1–3
Total non-methane organic compounds (TNMOC)	–	0.02–5	0.015–0.035	–	–	–	–	–	–
Metal ⁱ									
Antimony	Below detection limit	9.0E–06	9.0E–06	–	7000	–	- Eye and skin irritation - Harmful dust	5	1–2
Arsenic	9.5E–05	2.05E–04	2.05E–04	145	763	–	- Very toxic and may be fatal if contacted skin, inhaled and swallowed - Carcinogen	1, 4–5	1–2
Beryllium	1.55E–04	1.05E–05	1.05E–05	–	–	–	- Eye, skin and respiratory irritation - Carcinogen	–	1–3
Cadmium	3.55E–05	2.55E–05	2.55E–05	890	2330	–	- Eye and skin irritation - Harmful if swallowed and - May be fatal if inhaled - Carcinogen	5	1–2
Chromium	1.4E–02	1.3E–04	1.3E–04	–	–	–	- Eye, skin and respiratory irritation	5	1–2
Chromium(VI)	–	3.95E–05	3.95E–05	127	80	–	- Severe eye burns and - Respiratory irritation - Harmful if contacted skin and swallowed - Carcinogen	–	–
Cobalt	–	5.0E–05	5.0E–05	–	6171	–	- Eye and respiratory irritation - Carcinogen	5	1–2
Lead	4.45E–03	2.1E–04	2.1E–04	–	–	–	- Eye, skin and respiratory irritation - Carcinogen	1, 5	1–2
Magnesium	–	5.5E–03	5.5E–03	–	–	–	- Harmful dust	–	–
Manganese	1.8E–03	2.45E–04	2.45E–04	–	9000	–	- Eye, skin and respiratory irritation	5	1–2

Table 1 (Continued)

Substance (U.S. Environmental Protection Agency, 1995)	Emission (kg/Mg) (U.S. Environmental Protection Agency, 1995)			Toxicity ^a			Impact	Laws and regulation ^b	
	Anthracite coal	Bituminous-sub-bituminous coal	Lignite coal	LD ₅₀ -ORL (mg/kg)		Other toxicity		Canada	U.S.
				Mouse (MUS)	Rat (RAT)				
Mercury	6.5E-05	4.15E-05	4.15E-05	–	–	–	- Eye, skin and respiratory irritation and burns	1-5	1-3
Nickel	1.3E-02	1.4E-04	1.4E-04	–	–	250 mg/kg (IPR-RAT LD50)	- Eye and skin (severe) irritation - Carcinogen	5	1-2
Selenium	6.5E-04	6.5E-04	6.5E-04	–	6700	–	- Eye, skin and respiratory irritation - May be harmful if swallowed	5	1-2
Dioxin and furan ^j									
2,3,7,8-Tetrachlorodibenzo- p-dioxin (TCDD)	–	7.15E-12	–	–	–	–	–	1, 5	1
2,3,7,8-Tetrachlorodibenzofuran (TCDF)	–	2.55E-11	–	–	–	–	–	1, 5	–

^a Toxicology is obtained from MSDS (Fisher Scientific, Mallinckrodt Baker, Inc., Physical and Theoretical Chemistry Laboratory). The terminologies and abbreviations for toxicity information are expressed as listed; LD₅₀ (lethal dose 50% kill) is the dose large enough to kill 50% of a sample of animal under test and normally quoted as mg/kg where kg refers to body weight of the animal concerned. In general, the lower the LD₅₀ value, the higher the toxicity of the substance. LC₅₀ (lethal concentration 50% kill) is the concentration large enough to kill 50% of a sample of animal under a specified time. The lower the LC₅₀ value, the higher the toxicity of the substance. LD_{LO} (lowest published lethal dose) is the lowest dose of a substance that is reported to cause death in humans and animals and is usually lower than LD₅₀. The substance is introduced by any routes except inhalation over a specified time. LC_{LO} (lowest published lethal concentration) is the lowest concentration of a substance in air that is reported to cause death in humans and animals over a period of time either and is usually lower than LC₅₀. The substance is introduced by any routes except inhalation over a specified time either over 24 h for subacute and chronic effect or under 24 h for acute effect.

^b Canada: (1) Canadian Environmental Protection Act (CEPA) (excluding substances presented in non-domestic substances list (NDSL) and domestic substances list (DSL); (2) Great Lakes Binational Toxics Strategy (BTS); (3) Canada-Ontario Agreement Respecting the Great Lakes Basin Ecosystem (COA); (4) Toronto Sewer Use By Law (TSUBL); (5) National Pollutant Release Inventory (NRPI). The United States: (1) Clean Air Act (CAA); (2) Occupational Safety & Health Administration (OSHA); (3) [Resource Conservation and Recovery Act \(RCRA\)](#) (for P and U series).

^c A is ash content (wt%) of anthracite coal, bituminous-sub-bituminous coal (as fired) and lignite coal (wet basis).

^d Emission factors of PM are evaluated from uncontrolled combustors for anthracite coal and bituminous-sub-bituminous coal and from controlled combustors for lignite coal [baghouse, wet scrubber or electrostatic precipitator (ESP)].

^e S is sulphur content (wt%) of anthracite coal, bituminous-sub-bituminous coal (as fired) and lignite coal (wet basis). C is carbon content (wt%) of lignite coal (as fired).

^f Emission factors of CO₂, CO, NO_x, and SO_x are evaluated from uncontrolled combustors for anthracite coal and lignite coal.

^g Emission factors of HCl and HF are valid for both uncontrolled and controlled combustors for bituminous-sub-bituminous coal and lignite coal.

^h Emission factors of organic compounds are valid for both controlled bituminous-sub-bituminous coal combustors and controlled lignite coal combustors that utilize wet limestone scrubbers or spray dryers with a fabric filter (FF) or ESP, or utilize only a FF or ESP.

ⁱ Emission factors of metals are valid for both controlled bituminous-sub-bituminous coal combustors and controlled lignite coal combustors that utilize venturi scrubbers, wet limestone scrubbers or spray dryers with a FF or ESP, or utilize only a venturi scrubber, FF or ESP.

^j Emission factors of metals are valid for controlled bituminous-sub-bituminous coal combustors that utilize a FF or ESP.

Table 2 – Summary location and type of coal (Energy Information Administration, 2003, 2004)

Location	Anthracite	Bituminous	Sub-bituminous	Lignite
North America	The U.S. (Pennsylvania)	Canada, Mexico, The U.S. (Alabama, Arizona, Arkansas, Colorado, Illinois, Indiana, Kansas, Kentucky, Maryland, Missouri, New Mexico, Ohio, Oklahoma, Pennsylvania, Tennessee, Texas, Utah, Virginia, West Virginia, Wyoming)	Canada, The U.S. (Alaska, Colorado, Montana, New Mexico, Washington, Wyoming)	Canada, The U.S. (Louisiana, Mississippi, Montana, North Dakota, Texas)
Central and South America	Peru	Argentina, Brazil, Chile, Colombia, Venezuela	–	–
Africa	Morocco, South Africa, Swaziland	Botswana, Congo, Egypt, Mozambique, Niger, Nigeria, South Africa, Swaziland, Tanzania, Zambia, Zimbabwe	–	–
Europe	France, Germany, Poland, Russia, Spain, Ukraine, United Kingdom,	Belgium, Bosnia and Herzegovina, Bulgaria, Czech Republic, France, Germany, Kazakhstan, Kyrgyzstan, Norway, Poland, Romania, Russia, Slovenia, Spain, Tajikistan, Turkey, Ukraine, United Kingdom, Yugoslavia	–	Albania, Austria, Bosnia and Herzegovina, Bulgaria, Czech Republic, Estonia, France, Germany, Greece, Hungary, Kazakhstan, Kyrgyzstan, Macedonia, Poland, Romania, Russia, Slovenia, Spain, Turkey, Ukraine, Uzbekistan, Yugoslavia
Middle East	–	Iran	–	–
Asia and Oceania	China, South Korea, Vietnam	Australia, Bhutan, Burma, China, India, Indonesia, Laos, Malaysia, Mongolia, Nepal, North Korea, New Zealand, Pakistan, Philippines	–	Australia, Burma, China, India, Mongolia, North Korea, New Zealand, Philippines, Thailand

Table 3 – Emissions from various types of combustors (U.S. Environmental Protection Agency, 1995)

Types of coals	Emission	Combustor				
		Stoker-fired ^a	PC	FBC	Hand-fired ^a	Cyclone
Anthracite	PM	A ^b	High	–	Low	–
	SO _x	S ^c	S ^c	Low	–	–
	NO _x	Medium	High	Low	–	–
	CO ₂	–	–	–	–	–
	CO	Low	–	Low	–	–
Bituminous and sub-bituminous	PM	SF ^d	A ^b	–	Low	A ^b
	SO _x	S ^c	S ^c	S ^c	S ^c	S ^c
	NO _x	Low to medium	Low to high	Low to medium	Low	Medium to high
	CO ₂	CL ^e	CL ^e	CL ^e	CL ^e	CL ^e
	CO	Low	Low	Low	High	Low
Lignite	PM	A ^b	A ^b	A ^b	–	A ^b
	SO _x	S ^c	S ^c	S ^c	–	S ^c
	NO _x	Low	Medium to high	Low	–	High
	CO ₂	C ^f	C ^f	C ^f	–	C ^f
	CO	–	Low	Low	–	–

^a The most widely used combustor in industry.

^b A—the emission that depends on the ash content.

^c S—the emission that depends on the sulphur content.

^d Emission depending on types of stoker-fired boilers.

^e CL—the emission that depends on the coal types, i.e., sub-bituminous, high-volatile bituminous, medium-volatile bituminous, and low-volatile bituminous.

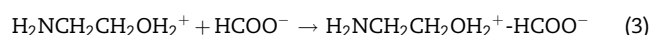
^f C—the emission that depends on the carbon content.

Apart from the typical alkanolamines mentioned above, there is also a large number of solvents currently proposed and being investigated. Some of them are proprietary. The Kansai Electric Company and Mitsubishi Heavy Industry (Mimura et al., 1995) developed a family of KS energy-efficient proprietary solvents. Many researchers have investigated the performance of hot potassium carbonate (K₂CO₃) plus DEA as an absorption rate enhancer (Savage et al., 1980; Tseng et al., 1988; Pohorecki and Kucharski, 1991). Recently, a group of researchers from the University of Texas at Austin have been testing the performance of blends between K₂CO₃ and piperazine (Cullinane and Rochelle, 2004). Ammonia (NH₃) has also been investigated for quite sometime (Huang et al., 2002).

3.2.2.2. Other chemicals. In addition to the absorption solvents, the process solution also contains degradation products and chemical additives such as corrosion inhibitors, antifoam agents, oxygen scavengers, and salt neutralizers. The degradation products are essentially formed by degradation reactions of the absorption solvents with other chemical constituents in the process solution. They can be either regenerable or non-regenerable under normal operating conditions of CO₂ stripping (or solvent regeneration) depending upon the types of chemical constituents taking part in the reactions. The degradation products caused by CO₂ are mostly regenerable and, hence, are not of great concern compared to the non-regenerable products. The non-regenerable degradation products, mainly heat-stable salts, are formed through the reactions of the absorption solvents with acids stronger than CO₂, such as carboxylic acids. Carboxylic acids are usually introduced to the capture process along with makeup water and feed gas streams or are generated within the process by chemical reactions with gaseous components such

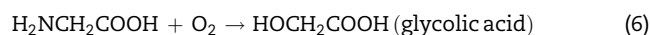
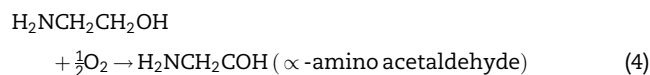
as O₂, CO, and SO₂. For example, formic and oxalic acids can be generated by the reactions of MEA with CO and O₂, respectively, as shown below.

Degradation by CO (Rooney et al., 1997):



where H₂NCH₂CH₂OH, HCOO[−], and H₂NCH₂CH₂OH₂⁺·HCOO[−] denote MEA, formate anion, and heat-stable formate salt of MEA, respectively.

Degradation by O₂ (not balanced) (McCullough and Nielsen, 1996):



where H₂NCH₂COH, H₂NCH₂COOH, HOCH₂COOH, HCOCOOH, and HOCOCOOH are α-amino acetaldehyde, glycine, glycolic acid, glyoxylic acid, and oxalic acid, respectively. A comprehensive list of degradation products compiled from literature (Kohl and Nielsen, 1997; Strazisar et al., 2003; Bello and Idem,

Table 4 – Summary of chemicals present in CO₂ capture unit

Chemical	LD ₅₀ -oral (mg/kg) ^a		Vapour pressure (mmHg) at 20 °C ^b	Impact	Laws and regulations ^c	
	Rabbit	Rat			Canada	The U.S.
Absorption solvents						
Monoethanolamine (MEA)	1,000	1,720	1000 (110 °C, 30 wt%) ^d	- Eye and skin burn - Moderate skin irritation - Harmful if contacted skin	–	2
Diethanolamine (DEA)	2,200	710	1000 (110 °C, 30 wt%) ^d	- Eye (severe), skin and respiratory irritation - May be harmful if swallowed	5	1
N-Methyldiethanolamine (MDEA)	–	1,945	950 (110 °C, 50 wt%) ^e	- Eye, skin and respiratory irritation	–	–
Diglycolamine (DGA)	–	3,000	900 (110 °C, 50 wt%) ^e	- Eye and skin burns - May be harmful if contacted skin	–	–
Diisopropanolamine (DIPA)	–	4,765	900 (110 °C, 60 wt%) ^e	- Eye, skin (mild) and respiratory irritation	–	–
2-Amino-2-methyl-1-propanol (AMP)	2,900	2,900	<1 (25 °C)	- Eye, skin and respiratory irritation	–	–
Hot potassium carbonate (HPC)	–	1,870	–	- Eye, skin and respiratory irritation - May be harmful if swallowed	–	–
Methanol	14,200	5,600	127 (25 °C)	- Moderate eye and skin irritation - Toxic if inhaled - Harmful if swallowed	5	1–3
n-Methyl-2-pyrrolidone (NMP)	–	3,914	0.5 (25 °C)	- Eye, skin (mild) and respiratory (mild) irritation	5	–
Propylene carbonate	–	–	0.00223 (25 °C)	- Eye and skin irritation	–	–
Selexol (dimethyl ethers of polyethylene glycol, DMPEG)	–	–	–	–	–	–
Sulphinol-D and sulphinol-M (mixture of DIPA or MDEA, water and sulpholane)	–	–	–	–	–	–
Oxygen scavengers (Veldman and Trahan, 1997, 2001)						
Oxime	–	–	–	–	–	–
Quinone	–	–	–	–	–	1–2
Hydroxylamine	–	–	–	–	–	–
Corrosion inhibitors (Mago and West, 1976; Veawab, 2000)						
Antimony						
Antimony powder	–	7,000	1 (886 °C), 5 (984 °C) ^f	- Harmful dust - Eye and skin Irritant	5	1–3
Potassium antimonyl tartrate	115	115	–	- Eye and skin Irritant - Harmful if swallowed and inhaled	–	–
Sodium antimonyl tartrate	–	–	–	–	–	–
Antimony pentachloride	–	1,115	1	- Eye and skin burns - Severe respiratory irritation - Harmful if inhaled	–	1
Vanadium						
Vanadium pentoxide	–	10	0.033 (700 °C)	- Eye, skin and respiratory irritation - May be fatal if swallowed - Carcinogen	–	2–3

Chemical	LD ₅₀ -oral (mg/kg) ^a		Vapour pressure (mmHg) at 20 °C ^b	Impact	Laws and regulations ^c	
	Rabbit	Rat			Canada	The U.S.
Sodium metavanadate	–	98	–	- Severe skin and eye irritation - Harmful if swallowed - Harmful dust	–	–
Sodium orthovanadate	–	330	–	- Eye, skin and respiratory irritation - Harmful if swallowed and inhaled	–	–
Ammonium metavanadate	–	58.1	–	- Eye, skin and respiratory irritation - Harmful if swallowed - May be fatal if inhaled	–	3
Sodium pyrovanadate	–	–	–	–	–	–
Sodium tetravanadate	–	–	–	–	–	–
Stannous salt						
Stannous chloride	–	700	5 (366 °C) ^f	- Eye and skin burns - Harmful if swallowed - May be harmful if inhaled	–	–
Stannous fluoborate	–	–	–	- Eye and skin burns	–	–
Stannic chloride	–	–	20 (22 °C)	- Severe eye, skin and respiratory irritation	–	–
Stannous tartrate	–	–	–	–	–	–
Stannous gluconate	–	–	–	–	–	–
Potassium stannate	–	–	–	–	–	–
n-Butylstannic acid	–	–	–	–	–	–
Benzotriazole	–	560	0.04	- Eye, skin and respiratory irritation - Harmful if swallowed	–	–
Copper						
Copper powder	–	–	1 (1628 °C)	- Eye and skin irritation - Harmful dust	5	–
Copper carbonate	159	1,350	–	- Eye (mild), skin and respiratory irritation - May be harmful if swallowed	–	–
Copper(II) acetate monohydrate	–	710	–	- Eye, skin and respiratory irritation - May be harmful if swallowed	–	–
Ammonium thiocyanate	–	750	–	- Eye (moderate), skin and respiratory irritation - Harmful if swallowed - May be harmful if contacted skin and inhaled	–	–
Cobalt compound	–	–	–	–	–	–
Salicylic acid	1,300	891	5 (136 °C)	- Severe eye irritation - Skin burns - May be harmful if swallowed	–	–
Ammonium hydroxide	–	350	557 (21 °C, 25%NH ₃)	- Severe eye and skin burns - Severe skin irritation - Harmful if swallowed	–	–
Potassium hydroxide	–	273	5 (814 °C)	- Eye (severe) and skin burns - Harmful if swallowed	–	–

Antifoams (Kohl and Nielsen, 1997; Ohta, 1982)						
Amino silicone	–	–	–	–	–	–
Dimethyl silicone	–	–	–	–	–	–
Oleyl alcohol	–	–	8 (195 °C) (70 wt%)	- Eye (mild), skin and respiratory irritation	–	–
Octylphenoxyethanol	–	–	–	–	–	–
Degradation products						
Heat-stable salts (Kohl and Nielsen, 1997; Strazisar et al., 2003; Bello and Idem, 2005; Rooney and DuPart, 2000)						
Acetic acid ^g	–	3,310	11–11.4	- Severe eye irritation - Skin burns - May be harmful if contacted skin	–	2
Bicine	–	–	–	- Eye, skin and respiratory irritation	–	–
Formic acid	–	1,100	33.55	- Severe eye and skin burns	5	2–3
N-Butyric acid ^g	–	2,000	0.43–0.84	- Eye and skin burns - Harmful if contacted skin - May be harmful if swallowed	–	–
Oxalic acid	–	7,500	0.92 (60 °C)	- Eye and skin (severe) burns - Harmful if contacted skin	–	2
Propionic acid ^g	–	2,600	2–10	- Severe eye and skin irritation and burns - Harmful if contacted skin	–	–
Acetate	–	–	–	–	–	–
Dithiocarbamate	–	–	–	–	–	–
Formate	–	–	–	–	–	–
Glycolate	–	–	–	–	–	–
Oxalate	–	–	–	–	–	–
Thiosulphate	–	–	–	–	–	–
Cations ^g (Strazisar et al., 2003)						
Aluminum	–	–	–	- Eye, skin and respiratory irritation	5	2
Arsenic	–	763	–	- Very toxic - May be fatal if contacted skin, inhaled and swallowed - Carcinogen	1, 4–5	1–2
Calcium	–	–	10 (983 °C)	- Eye, skin and respiratory irritation	–	–
Copper	–	–	1 (1628 °C), 5 (1795 °C) ^f	- Eye and skin irritation - Harmful dust	5	2
Iron	–	30,000	1 (1787 °C)	- Skin irritation	–	–
Potassium	–	–	10 (983 °C) ^f	- Eye and skin burns - Respiratory irritation	–	–
Selenium	–	6,700	–	- Eye, skin and respiratory irritation - May be harmful if swallowed	5	1–2
Sodium	–	–	1 (440 °C)	- Severe eye and respiratory irritation - Skin burns	–	–
Zinc	–	–	1 (487 °C)	- Eye and skin irritation	–	–
Anions ^g (Strazisar et al., 2003)						
Bromide	–	–	–	–	–	–
Chloride	–	–	–	–	–	–
Fluoride	–	–	–	–	–	–
Nitrate	–	–	–	–	–	–

Table 4 (Continued)

Chemical	LD ₅₀ -oral (mg/kg) ^a		Vapour pressure (mmHg) at 20 °C ^b	Impact	Laws and regulations ^c	
	Rabbit	Rat			Canada	The U.S.
Nitrite	–	–	–	–	–	–
Phosphate	–	–	–	–	–	–
Sulphate	–	–	–	–	–	–
Other degradation products (Kohl and Nielsen, 1997; Strazisar et al., 2003; Bello and Idem, 2005; Malcolm and Meisen, 1985; Dawodu and Meisen, 1994; Jamal and Meisen, 2001) (with toxicology and/or laws and regulations)						
1,2-Ethanediol	–	4,700	0.08	- Skin and respiratory irritation - Harmful if swallowed - May be harmful if contacted skin and inhaled	5	1
1,3-Dioxane	–	–	39 (25 °C)	- Eye, skin and respiratory irritation - May be harmful if contacted skin	–	–
1-Amino-2-propanol	–	1,715	0.47 (25 °C)	- Severe eye and respiratory irritation - May be harmful if contacted skin and swallowed	–	–
1H-imidazole	1,130	–	0.478 (25 °C)	- Eye and skin burns - May be harmful if swallowed	–	–
1-Piperazineethanol or N-(2-hydroxyethyl)piperazine (HEP)	3,350	–	–	- Eye, skin and respiratory irritation	–	–
1-Propanamine	–	370	308 (25 °C)	- Severe eye, skin and respiratory irritation - Harmful if contacted skin, inhaled and swallowed	–	3
2-(2-Ethoxyethoxy)ethanol	3,620	7,500	0.14	- Eye, skin (mild) and respiratory irritation - May be harmful if swallowed	–	1
2-Butanamine	–	152	135	- Severe eye and skin burns - Harmful if swallowed - Very harmful to aquatic organisms	–	–
2-Methyl-1H-imidazole	–	–	<0.75	- Eye and skin burns - Harmful if swallowed	–	–
2-(Methylamino)ethanol	–	1,391	0.52	- Eye (severe) and skin irritation - Harmful if contacted skin	–	–
2-Oxazolidone ⁸	–	–	–	- Skin, eye and respiratory irritation	–	–
2-Pyrrolidinone	–	328	–	- Eye, skin and respiratory irritation - Harmful if swallowed	–	–
3-Amino-1-propanol	–	–	–	- Eye and skin burns - May be harmful if contacted skin	–	–
3-Methylpyridine	–	400	6.05 (25 °C)	- Eye, skin (severe) and respiratory irritation - Harmful if swallowed - May be harmful if contacted skin	–	–
4-Methylmorpholine	–	1,960	13.2 (25 °C)	- Eye and skin burns - May be harmful if inhaled and swallowed	–	–
12-Crown-4	–	2,830	–	- Eye, skin and respiratory irritation	–	–
15-Crown-5	–	1,410	–	- Eye and skin irritation - May be harmful if swallowed	–	–

Acetamide	–	7,000	–	- Eye, skin (mild) and respiratory irritation - Carcinogen	–	1
Acetone	5,340	5,800	231 (25 °C)	- Eye and respiratory irritation	–	2–3
Ammonia (solution) ^g	–	350	557 (21 °C, 25%NH ₃)	- Severe eye and skin burns - Severe skin irritation - Harmful if swallowed	–	2
Butanone	–	2,737	77.5	- Eye and respiratory irritation	5	2–3
Ethoxyethene	–	273	428	- Eye, skin and respiratory irritation	–	–
Ethylamine	–	–	–	- Eye, skin and respiratory irritation - Harmful if inhaled and swallowed	–	2
Ethylaminoethanol (EAE)	–	1,000	–	- Eye and skin burns - Harmful if contacted skin	–	–
Ethyl-diethanolamine	–	4,570	–	- Eye, skin (mild) and respiratory irritation	–	–
Ethylenediamine	–	500	10	- Harmful if contacted skin, inhaled and swallowed	–	2
N-Acetyldiethanolamine ^g	–	26,950	–	- Eye, skin and respiratory irritation	–	–
Uracil	>10,000	>6,000	–	- Eye, skin and respiratory irritation	–	–

Without toxicology and/or laws and regulations

1,2,3,6-Tetrahydro-1-nitrosopyridine, 1,3,4-dehydropyrrolidine, 1,3,5-triazine, 1,4,7,10,13,16-hexaoxacyclooctadecane, 1-(2-hydroxyethyl)-2-imidazolidinone^g, 1-butyl-5-methyl-2-pyrazoline, 1H-imidazole-4-carboxylic acid methyl ester, 1-hydroxyethyl-2-piperazine^g, 1-hydroxyethyl-3-homopiperazine^g, 1-methyl-1H-imidazole-2-methanol, 1-methyl-2,4-imidazolidinedione, 1-methyl-2-imidazolecarboxaldehyde^g, 1-methylazetidine, 2,2-dimethyl-3(2H)-furanone, 2,3-dihydro-1-methyl-4(1H)-pyridinone, 2,4-dihydro-4,5(3H)-pyrazol-3-one, 2,6-dimethyl-4-pyridinamine^g, 2,6-dioxatricyclo[3,3,2,0-(3,7)]dec-9-ene, 2-ethenyl-1H-imidazole, 2-hydroxyethylamino-N-hydroxyethylacetamide^g, 2-imidazolecarboxaldehyde^g, 2-propanone oxime, 2-quinazolinamine, 3,3-(1,2-ethanediyl)bis(sydnone), 3,4-dehydro-DL-proline, 3-cis-5-heptadien-1-ol, 3-hydroxyethylamino-N-hydroxy-ethylpropanamide^g, 3-(hydroxyethyl)-2-oxazolidone (HEOD), 3-methyl-1,2-cyclopentanedione, 3-methyl-4-amino-4,5(1H)-dihydro-1,2,4-triazol-5-one, 3-methylcyclopentanol, 4-ethylcyclohexene, 4-ethylquinoline, 4-(hydrazinocarbonyl)imidazole, 4-hydroxyethyl-2-piperazine^g, 5-(hydrazinocarbonyl)imidazole, 6-hydroxy-4(1H)-pyrimidinone, 7-oxabicyclo[2.2.1]hept-5-en-2-one, [(aminocarbonyl)amino]oxo-acetic acid, bis(hydroxyethylaminoethyl)ether, carboxy-BHEED, carboxy-THEED, carboxydiethanolamine, carboxymonoethanolamine, diethanolammonium, N,N-bis-(2-hydroxyethyl)dithiocarbamate, (dimethylamino)ethylidene-*tert*-butylamine, ethanethioic acid S-(hydroxyethyl)-aminomethyl ester (ETAHEAME), ethoxyethylamine, formyl-diethanolamine (DEAF), (hydroxyethyl)acetamide, methylpyrazine, N-(2-hydroxyethyl)acetamide^g, N-(hydroxyethyl)-ethylenediamine (HEED), N-(2-hydroxyethyl)-lanthamide^g, N-(2-hydroxyethyl)succinimide, N-butylformamide, N-formylethanolamine^g, N-formyl-N-methylformamide, N-(hydroxyethyl)ethyleneimine (HEM), N-(hydroxyethyl)imidazolidone (HEI), N-(hydroxyethyl)succinimide^g, N,N-bis(hydroxyethyl) ethylenediamine (BHEED), N,N'-bis(hydroxyethyl) imidazolidone (BHEI), N,N'-bis(hydroxyethyl)piperazine (BHEP), N,N-diethylurea, N,N,N'-tris(2-hydroxyethyl)ethylenediamine (THEED), N,N,N',N'-tetrakis(2-hydroxyethyl)-thiocarbamide, N,N,N,N'-tetra(hydroxyethyl)ethylenediamine (TEHEED), nitrosomethane, trimethylhydrazine

^a LD₅₀ obtained from MSDS (Fisher Scientific, Mallinckrodt Baker, Inc., Physical and Theoretical Chemistry Laboratory).

^b Vapour pressure obtained from MSDS (Fisher Scientific, Mallinckrodt Baker, Inc., Physical and Theoretical Chemistry Laboratory).

^c Canada: (1) Canadian Environmental Protection Act (CEPA) (excluding substances presented in non-domestic substances list (NDSL) and domestic substances list (DSL); (2) Great Lakes Binational Toxics Strategy (BTS); (3) Canada-Ontario Agreement Respecting the Great Lakes Basin Ecosystem (COA); (4) Toronto Sewer Use By Law (TSUBL); (5) National Pollutant Release Inventory (NPRI). The United States: (1) Clean Air Act (CAA); (2) Occupational Safety & Health Administration (OSHA); (3) Resource Conservation and Recovery Act (RCRA) (for P and U series).

^d Vapour pressure obtained from Dow Chemical Company (1962).

^e Vapour pressure obtained from Kohl and Nielsen (1997).

^f Vapour pressure obtained from Perry's chemical engineers' handbook (Perry et al., 1997).

^g Degradation product analyzed from plant sample (Strazisar et al., 2003).

Table 5 – Typical concentrations of heat-stable salt anions found in amine treating units

HSAS type	Range (ppmw)	References (Fan et al., 2000; Liu and Dean, 1995; Craig and McLaughlin, 1996; Litchewski, 1996)	Note
Acetate	0–1,500	Fan et al. (2000)	DEA solution in refinery (vendor data)
	5,000	Liu and Dean (1995)	MDEA solution in refinery (plant sample)
	2,406–3,789	Liu and Dean (1995)	MDEA solution in refinery (plant sample)
	750–1,250	Craig and McLaughlin (1996)	DEA solution in refinery (plant sample)
Formate	0–35,000	Fan et al. (2000)	DEA solution in refinery (vendor data)
	15,000–17,000	Fan et al. (2000)	DEA solution in refinery (vendor data)
	5,000–7,000	Fan et al. (2000)	DEA solution in refinery (vendor data)
	25,000–30,000	Fan et al. (2000)	DEA solution in refinery (vendor data)
	5,000–15,000	Fan et al. (2000)	DEA solution in refinery (vendor data)
	500–11,900	Litchewski (1996)	MDEA solution in refinery (plant sample)
	45,000	Liu and Dean (1995)	MDEA solution in refinery (plant sample)
	10,474–57,747	Liu and Dean (1995)	MDEA solution in refinery (plant sample)
Glycolate	0–150	Fan et al. (2000)	DEA solution in refinery (vendor data)
	6,000–21,000	Craig and McLaughlin (1996)	DEA solution in refinery (plant sample)
Oxalate	0–150	Fan et al. (2000)	DEA solution in refinery (vendor data)
	100	Liu and Dean (1995)	MDEA solution in refinery (plant sample)
Sulphate	0–350	Fan et al. (2000)	DEA solution in refinery (vendor data)
	100	Liu and Dean (1995)	MDEA solution in refinery (plant sample)
Thiosulphate	0–700	Fan et al. (2000)	DEA solution in refinery (vendor data)
	600	Liu and Dean (1995)	MDEA solution in refinery (plant sample)
Thiocyanate	0–3,000	Fan et al. (2000)	DEA solution in refinery (vendor data)
	500–1,000	Fan et al. (2000)	DEA solution in refinery (vendor data)
	2,000–3,500	Fan et al. (2000)	DEA solution in refinery (vendor data)
	500–1,000	Fan et al. (2000)	DEA solution in refinery (vendor data)
	1,000–3,000	Fan et al. (2000)	DEA solution in refinery (vendor data)
	3,500	Liu and Dean (1995)	MDEA solution in refinery (plant sample)
	883–21,462	Liu and Dean (1995)	MDEA solution in refinery (plant sample)

2005; Rooney and DuPart, 2000; Malcolm and Meisen, 1985; Dawodu and Meisen, 1994; Jamal and Meisen, 2001) is also given in Table 4. Concentrations of common heat-stable salts found in amine treating plants are listed in Table 5.

The presence of heat-stable salts in the process solution causes a number of adverse effects, including a reduction in acid gas absorption capacity of amine, an increase in solution viscosity, an increase in foaming tendency of the solution, a reduced filter runtime due to the solid precipitation in the solution, and an increase in corrosion (Rooney and DuPart, 2000; Tanthapanichakoon et al., 2006). Addition of an oxygen scavenger to the solution is claimed to reduce the formation of heat-stable salts. Examples of oxygen scavengers are oxime, quinone, hydroxylamine, and their mixtures (Veldman and Trahan, 1997, 2001).

Table 4 also provides a list of corrosion inhibitors (Mago and West, 1976; Veawab, 2000), which have been developed, patented, and/or commercialized by many major chemical companies for use in CO₂ absorption plants. The patented organic inhibitors include thiourea and salicylic acid, while the inorganic inhibitors are vanadium, antimony, copper, cobalt, tin, and sulphur compounds. The inorganic inhibitors are, in practice, more favoured than the organic ones because of their superior inhibition performance. Vanadium compounds, particularly sodium metavanadate (NaVO₃), are the most extensively and successfully used in amine treating plants.

In addition, antifoam agents are often used for reducing foam formation, which may occur due to the presence of fine

solid particles and heat-stable salts. Common antifoam agents are high-boiling alcohols (Kohl and Nielsen, 1997), such as oleyl alcohol and octylphenoxylethanol, or silicone-based compounds (Ohta, 1982) such as amino silicon and dimethyl silicon.

4. Emissions and their impacts

Pollutant emissions potentially harming human health and the environment are essentially from two sources in CO₂ capture processes, point of discharge and fugitive emissions. The emissions from the point of discharge are intentional, predictable, and quantifiable based on plant's operating conditions. Such emissions are the treated gas released from the absorber top and the waste of process solution released from solution reclamation or other purification units. Fugitive emissions are unintentional releases from process equipment and piping during plant operation. Details of these emissions are given below.

4.1. Point of discharge

4.1.1. Treated gas

A CO₂ capture unit releases the treated gas from the absorber top to the atmosphere on a continuous basis. The treated gas is basically composed of the flue gas with a reduced CO₂ content and vapours of process solution. As mentioned previously

(Section 3.2.1), the flue gas entering the CO₂ capture unit contains a great number of substances. Most of these substances, by themselves, have significant impacts on human health and the environment, and they are currently controlled under the environmental laws and regulations (Table 1). Most gaseous components, including CO, HCl, HF, NO_x, and SO_x, are toxic. From MSDS, the organic compounds resulting in detrimental carcinogenic damage include benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, naphthalene, acetaldehyde, benzene, benzyl chloride, bis(2-ethylhexyl)phthalate, chlorobenzene, chloroform, 2,4-dinitrotoluene, dimethyl sulphate, ethyl benzene, ethyl chloride, ethylene dichloride, ethylene dibromide, formaldehyde, isophorone, methyl bromide, methyl chloride, methyl hydrazine, methyl *tert*-butyl ether, methylene chloride, tetrachloroethylene, styrene, and vinyl acetate. In addition, trace metals, such as arsenic, beryllium, cadmium, chromium, cobalt, lead, and nickel, are toxic and also carcinogenic.

In Canada, PM, NO_x, and SO₂ are controlled under CEPA (Canada Gazette Part III, 1999; Canada Gazette Part I, 2001). Most organic compounds mentioned above are regulated, with the exception of acenaphthene, acenaphthylene, acetaldehyde, acrolein, benzene, biphenyl, DEHP, ethylene dichloride, fluorene, and 5-Methylchrysene, methyl bromide, methylene chloride, tetrachloroethylene, and 1,1,1-trichloroethane. In addition, some trace metals, arsenic, cadmium, chromium(VI), lead, and mercury, together with dioxin and furan, are also regulated.

In the United States, PM, NO_x, and SO₂ are regulated under CAA. Recently, the Clean Air Mercury Rule was established to reduce the emission of mercury from coal-fired power plants. Most organic compounds are listed as hazardous air pollutants (e.g., acetaldehyde, acetophenone, acrolein, benzene, biphenyl, bis(2-ethylhexyl)phthalate, naphthalene, and propionaldehyde) (Clean Air Act). Some metals (e.g., arsenic, beryllium, lead, and mercury) are considered as hazardous air pollutants (Clean Air Act).

Despite their adverse impacts, flue gas substances are not considered to be contributors to any environmental impacts caused by the CO₂ capture unit integrated to the power plant. This is because these flue gas substances are intrinsically and originally produced from the coal combustion regardless of the installation of a CO₂ capture unit. Vapours of process solution are, however, considered to be the actual emissions resulting from the CO₂ capture unit.

The emission of process solution vapours greatly depends on the operating conditions of the absorber top and the thermodynamic properties (that is vapour pressure) of the chemicals contained in the process solution. As an example, the vapour pressure of MEA is a function of absorber temperature (at the top) and chemical concentration (i.e., it increases with increasing MEA concentration and temperature). Any substance with high vapour pressure tends to vaporize and leave the top of the absorber very easily with the treated gas. A water wash and/or a well-designed mist eliminator are commonly installed at the top section of the absorber to reduce such entrainment and volatility loss.

According to the vapour pressures, also listed in Table 4 for each chemical, besides water vapour, vapours of certain

absorption solvents and degradation products can be released from the absorber top, but the release of corrosion inhibitors is considered negligible due to the extremely low partial pressure of the compounds. The primary amine MEA tends to cause greater solvent volatility loss than other alkanolamines but still less than methanol. By average, the entrainment can lead to the emission of up to 8.5 mg amine/N m³ of treated gas (Veldman, 1989), and the total solvent loss is about 1.6 kg solvent/tonne CO₂ for gas-fired flue gas (Chapel and Mariz, 1999). The entrained vapours of absorption solvents should cause low toxicity to human health and the environment due to their diluted concentrations in the atmosphere. The level of exposure depends on many factors, including environmental, geographic, or atmospheric conditions, which can affect the distribution and dispersion of pollutants from the source of discharge into the air. The U.S. laws regulate MEA by OSHA and DEA by NESHAP, while the Canadian laws control DEA as “need to be declared” in NRPI. The other solvents are not enforced by any laws.

The degradation products, including formic acid, 1-propanamine, 2-butanamine, acetone, ammonia, butanone, and ethoxyethene, also have a tendency to vaporize and entrain with the treated gas, since their vapour pressures are higher than the vapour pressure of water at 20 °C. It was found that 2-butanamine, ammonia and ethylamine, are fairly toxic and can affect human health through skin burns and irritation. From MSDS, 2-butanamine is also reported to be very harmful to aquatic organisms. However, 2-butanamine, ammonia, and ethoxyethene are currently not regulated under any laws, while the rest are enforced by U.S. laws. Formic acid and butanone are controlled under Canadian laws.

4.1.2. Waste of process solution

According to general practice for gas treating processes, a side-stream of process solution must be purified to remove suspended solids, degradation products, and other process contaminants so that the concentration of active absorption solvents can be maintained. The solution purification is carried out through continuous adsorption, using mechanical and activated carbon filtration, and periodic thermal reclaiming. The filtration removes solid contaminants and large molecules of degradation products. As such, it results in routine disposal of wastes in the form of filter sludge/filter waste products, filter bag, cartridge, suspended solids, and used activated carbon. The thermal reclaiming is in operation to remove heat-stable salts, non-volatile organics, and suspended solids via a side-stream 0.5–2% of process solution (Kohl and Nielsen, 1997). The reclaiming operation will be performed when the content of heat-stable salt anions in the process reaches 1.2 wt% of solution (CCR Technologies Inc.) or when the degradation product exceeds 10 wt% of active alkanolamine solvents (Kohl and Nielsen, 1997). This generates a reclaimer waste comprising mostly heat-stable salts and solid precipitates and also comprising small amounts of absorption solvents, corrosion inhibitor, and other additives (Table 4). As an example, approximately 0.003 m³ of reclaimer waste per tonne of CO₂ captured was produced in a commercial FG Econamine process (Chapel and Mariz, 1999). Examples of reclaimer waste samples and their concentrations obtained from the IMC Chemical Facility in Troca, CA in

Table 6 – List of chemicals in process waste and their discharge from reclaimer (Strazisar et al., 2003; Schnell et al., 2004)

Chemicals	Concentration (wt%)
Cation	
Sodium	0.08210
Potassium	0.00180
Calcium	0.00013
Iron	0.00011
Copper	0.00001
Zinc	0.00002
Aluminum	0.00004
Selenium	0.00174
Arsenic	0.00017
Anion	
Fluoride	0.15000
Chloride	4.90000
Bromide	0.00800
Sulphate	0.02500
Nitrate	0.3100
Nitrite	Trace
Phosphate	0.02300
Absorption solvents + other degradation products + metals from equipment corrosion + charcoal from solvent filters	94.49790
Total	100

1998 are summarized in Table 6 (Strazisar et al., 2003; Schnell et al., 2004).

Among the chemicals present in the reclaimer wastes, heavy-metal corrosion inhibitors make the process waste toxic to humans and the environment. According to the Environmental Protection Agency (EPA), corrosion inhibitors containing vanadium, antimony, and cyanide compounds are considered hazardous substances, and they are priority/toxic pollutants under the CAA and also considered hazardous wastes under RCRA. In Canada, uses of toxic substances, including several inorganic heavy metals, are controlled under CEPA. Many countries and regions around the world are introducing a series of controlling regulations to provide guidelines on the use and discharge of these toxic substances, especially inorganic salts and salts of heavy metals. In Europe, for example, the European Union (EU) has charged the Paris Commission (PARCOM) with providing a framework for legislation (Haslegrave et al., 1992; McMahon and Harrop, 1995). Other highlighted regulations include the Emergency Planning and Community Right to Know Act of 1986, regulations adopted by the US Occupational Safety and Health Administration (OSHA) in 1993, and adoption of the Chemical Hazard Assessment and Risk Management (CHARM) model in the UK and other European countries (Singh and Bockris, 1996). Because of the adopted regulations, use of toxic corrosion inhibitors makes disposal of the industrial waste difficult and costly (Kohl and Nielsen, 1997; Singh and Bockris, 1996). Restriction on the use of other heavy-metal inhibitors can be anticipated in the near future. Arsenic is a good example of the corrosion inhibitors; it was used effectively in gas treating plants but is now banned from industrial applications due to its high toxicity and impacts on the environment.

Some degradation products, especially heat-stable salts and cations, are being regulated under laws and regulations. Their impacts are mostly irritation and burns. However, there are no regulations to control the emissions of such degradation products with high toxicity as 1H-imidazole, 2-butanimine, and 2-methylpropanenitrile.

The process wastes are generally disposed of by incineration and landfill. Incineration involves the supply of energy and the phase change of wastes either from solid to liquid or gas or from liquid to gas. As a result, burning the process wastes produces ashes of both degradation products and additives together with vapours of amine solvents. Some of these products are harmful to humans and the environment, as described previously. To reduce the release of trace metals, a post-treatment of incineration (i.e., wet scrubber) should be used. In contrast to incineration, placing the process wastes in landfills does not result in phase change of wastes, thus minimizing the emission of vapours of any toxic substances. Nevertheless, the process wastes should be neutralized prior to disposal in landfills.

4.2. Fugitive emissions

Fugitive emissions also contribute to environmental impacts in addition to the above point-source emissions. During plant operation, the process fluids can be unintentionally released from the CO₂ capture unit mainly through leaks, which are usually a consequence of deterioration of process equipment and pipes, corrosion, impact damage, and vibration. Such emissions are unpredictable, random, intermittent, and can occur everywhere on the site, such as at pumps, valves, flanges, connectors, pressure relief devices, sampling connections, open-ended lines, instruments, vents, drains, and meters. According to the European Sealing Association (ESA) (2005), for any commercial plants, valves, especially control valves, contribute the greatest to leakage losses (50–60%), followed by relief valves (15%), tanks (10%), pumps (10%), and flanges (5%).

Apart from leakage losses, working and breathing losses are also account for some fugitive emissions. Working loss occurs when the storage tanks of absorption solution are being filled. The quantity of solution vapour released from the tanks depends on temperature, vapour pressure of the solution, and pumping rate. Breathing losses are caused by thermal expansion of the solution vapour in the tanks as a result of temperature increase during the daytime. Regardless of their sources, fugitive emissions release certain amounts of process fluids and materials, including untreated flue gas, treated gas, absorption solvents, corrosion inhibitors, degradation products, and chemical additives, whose impacts to humans and the environment were previously discussed. The importance of fugitive emission has been recognized in environmental laws and regulations.

4.3. Accidental release

Accidental release is a large release, spill, or discharge of process fluids as a result of accidents and emergency operations. The quantities of such releases are much larger than that of the fugitive emissions. According to the American

Table 7 – Emission and waste from CO₂ capture process

Specifications of CO ₂ capture process		
CO ₂ content in feed gas (%)		12
CO ₂ removal efficiency (%)		90
Removal capacity (tonne CO ₂ /day)		1000
Absorption solvent		MEA
Solvent concentration (wt%)		30
CO ₂ lean loading of the absorption solvent (mol/mol)		0.20
CO ₂ rich loading of the absorption solvent (mol/mol)		0.45
Slip stream to reclaimer (%)		0.5–2.0
Concentration of total heat-stable-salts entering reclaimer		10% of active amine
Ratio of individual heat-stable salts to total amount of salts (fraction) (Liu and Dean, 1995)		
Formate		87.0
Acetate		4.6
Thiosulphate		1.2
Thiocyanate		6.8
Oxalate		0.2
Sulphate		0.2
Concentration of corrosion inhibitor in amine solution (ppm)		500
Reclaimer waste (kg/tonne CO ₂ captured)	0.5% slip stream	2.0% slip stream
Total	3.729	14.917
Formate	0.926	3.702
Acetate	2.417	9.668
Thiosulphate	0.129	0.516
Thiocyanate	0.032	0.129
Oxalate	0.188	0.752
Sulphate	0.005	0.021
Corrosion inhibitor	0.005	0.021
	Without water-wash	With water-wash
Treated gas (kg/tonne CO ₂ captured)		
MEA emission at 20 °C	0.11	–
MEA emission at 30 °C	0.32	0.03
MEA emission at 40 °C	0.72	–
Treated gas (if 50 wt% DEA solution is used)		
DEA emission at 20 °C	0.01	–
DEA emission at 30 °C	0.02	–
DEA emission at 40 °C	0.05	–
Fugitive emissions (kg/tonne CO ₂ captured) (Allen and Shonnard, 2001)		
Pressure relief devices (American Petroleum Institute (API), 2001)		4.08×10^{-3} (62.6%)
Valves (European Sealing Association (ESA), 2005)		1.55×10^{-3} (23.7%)
Pump seals		4.58×10^{-4} (7.0%)
Flanges and connectors (European Sealing Association (ESA), 2005)		3.58×10^{-4} (5.5%)
Open-ended lines (European Sealing Association (ESA), 2005)		7.99×10^{-5} (1.2%)
Storage tanks		4.96×10^{-7} (0.01%)

Petroleum Institute (API) (2001), accidental release can be caused by failures of process equipment due to physical erosion, wear and tear, corrosion, malfunctions of process controls and instrumentation that lead to overpressure, overheatings, and liquid overflow, as well as improper operations that lead to foaming, pluggings or blockage of process equipment and piping.

5. Emission distribution: a case study

As previously discussed, the substances potentially causing adverse environmental impacts are discharged from the absorber with the treated gas, from the reclaimer with the slurry waste, from fugitive emission sources, and, in rare cases, from the accidents. The quantities of these emissions

(except for accidental release) were determined by considering an absorption plant for capturing CO₂ from coal-fired flue gas with the specifications given in Table 7. The calculation results show that the reclaimer waste is the largest in size and contributes the most to environmental impacts due to the presence of corrosion inhibitor and heat-stable salts. The quantity of reclaimer waste varies with a ratio of slip stream to total circulation rate of process solution. A higher slip stream ratio leads to more waste produced. For instance, 2% slip stream generates 14.92 kg waste/tonne of CO₂ captured, while 0.5% slip stream reduces the waste discharge to 3.73 kg/tonne of CO₂. It should be noted here that, although only a trace of amine was designed to be discarded from the reclaimer in this work, a noticeable amount of amine can also be anticipated, depending on the design and operation of the reclaimer.

The treated gas discharge contains vapours of amine solvents and some degradation products whose quantities and impacts are small compared to the reclaimer waste. The quantities of these discharges depend on the temperature of absorber top and the efficiency of water-wash section. For instance (Table 7), in the case of CO₂ capture using 30 wt% MEA solution, an emission of MEA vapour increases from 0.11 to 0.72 kg/tonne CO₂ when temperature of the absorber top raises from 20 to 40 °C without water-wash operation. Such levels of MEA emission can substantially decrease, to about 0.03 kg/tonne CO₂ (or 0.5 lb/MMscf treated gas), when a proper design absorber with a well-designed water-wash section is in service. A similar result was also found in the case of 50 wt% DEA solution. However, the emission of DEA is much less than that of MEA due to the vapour pressure value.

Fugitive emission is the smallest portion and contributes the least compared to the other two discharges. The emission estimation accounted for all common fugitive sources reported in chemical plants. The pressure relief valves were found to be the largest fugitive source, followed by valves, pump seals, flanges/connectors, open-ended lines, and storage tanks.

6. Management of pollutant releases and their impacts

Although the impacts of a CO₂ capture unit integrated to the power plant is not severe, an Environmental Management System (EMS) should be practiced to control pollution, minimize waste production, ensure progress toward an environmental goal, and provide safety plans for normal plant operation and accidents. The EMS requires a commitment from top management to establish a corporate environmental management policy and educate employees on the

policy (Crognale, 1999). Proper operation, monitoring, and maintenance of process equipment, piping, and instrument and control systems play a key role in reducing emissions of hazardous substances from process points of discharge, fugitive sources, and accidental events. Pipeline and tube bundles in the heating elements should be regularly monitored, due to deterioration by corrosion. Trays or packings in both absorber and regenerator should be kept clean from sludge deposit. The amounts of heat-stable salts or any particulates in the process solution must be kept low to avoid foaming problems, which is a primary cause of entrainment at the absorber top. Immediate repair, replacement, and modification of the existing equipment must be done promptly when the damage is identified. Several publications provide guidelines for amine plant operations. Bacon (1987) recommended tests on lean- and rich-amine solution loadings, total heat-stable salts, anion and cation assay, soluble iron content of solution, degradation products, and foaming tendency (Bacon, 1987). Pauley (1991) suggested that the amine solution should be sampled and tested regularly for organic acids, heat-stable salts, amine concentration, soluble metal content, iron sulphide content, liquid hydrocarbon content, and water content (Pauley, 1991). Nielsen et al. (1995) provided a set of maximum concentrations of heat-stable salts that should be kept to prevent severe corrosion (e.g., 250 ppm for oxalate; 500 ppm for formate, glycolate, malonate, sulphite, and sulphate, 1000 ppm for succinate; and 10,000 ppm for thio-sulphate) (Nielsen and Lewis, 1995). The recommendations for leakage reduction from these process components are summarized in Table 8.

Standard plans for the worst and the most likely emergency scenarios should also be developed to effectively and immediately mitigate accidental release. Such plans must at least provide proper procedures for handling the release and clean up of hazardous pollutants and must be distributed to and well understood by both plant employees and local authorities, such as local police, fire fighters, and hospitals.

Table 8 – Equipment modifications for control of equipment leak (European Sealing Association (ESA), 2005)

Equipment	Modification
Valves	Sealless design Avoid using valves with rising stem (gate valves and globe valves) Install the rupture discs before the safety valve to damp small pressure fluctuation
Pump seals	Sealless design Closed-vent system Dual mechanical seal with barrier fluid maintained at a higher pressure than the pumped fluid
Flanges and connectors	Weld together Correct selection and installation of the gasket and regular maintenance Minimize the number of flanged connection
Pressure relief devices	Closed-vent system Rupture disk assembly
Open-ended lines	Blind, cap, plug, or second valve

7. Conclusions

Integration of a CO₂ capture unit to coal-fired power plant leads to environmental benefit through reduction of greenhouse gas emissions to the atmosphere. However, it may create mild impacts and unintentional burdens on human health and the environment through four pathways, including treated gas, reclaimer waste, fugitive emissions, and accidental release. Among the first three pathways, reclaimer waste is the largest in quantity and contributes the highest impacts due to the presence of heavy metal corrosion inhibitors and heat-stable salts. Treated gas contributes less because it contains amine solvents and some types of degradation products but not corrosion inhibitors. Fugitive emissions are the smallest and contribute the least to the environmental impacts. The impacts can be predetermined and properly mitigated through a well-established environmental management program and mitigation measures. Use of more environmentally friendly chemicals, especially as corrosion inhibitors and other additives, is also encouraged.

Acknowledgement

The authors gratefully acknowledge the Natural Sciences and Engineering Research Council of Canada (NSERC) for its financial support.

REFERENCES

- Allen, D.T., Shonnard, D.R., 2001. *Green Engineering: Environmentally Conscious Design of Chemical Processes*. Prentice Hall, NJ, USA.
- American Petroleum Institute (API), 2001. Recommended practice for analysis, design, installation and testing of basic surface safety systems for offshore production platforms. API Recommended Practice 14C.
- Bacon, T.R., 1987. Amine solution quality control through design, operation and correction. In: *Proceedings-1987 Gas Conditioning Conference*, The University of Oklahoma, Norman, Oklahoma.
- Bello, A., Idem, R.O., 2005. Pathways for the formation of products of the oxidative degradation of CO₂-loaded concentrated aqueous monoethanolamine solutions during CO₂ absorption from flue gases. *Ind. Eng. Chem. Res.* 44, 945–969.
- Clean Air Act. Section 111: standards of performance of new stationary sources (40CFR60, subpart D and Da).
- Clean Air Act. Section 112: national emission standards for hazardous air pollutants (40CFR63).
- CCR Technologies Inc. Solvent Quality Guidelines (Technical Bulletin).
- Canada Gazette Part III, 1999. Canadian Environmental Protection Act (CEPA), vol. 22, no. 3 (Chapter 33).
- Canada Gazette Part I, 2001. Notice with respect to substances in the National Pollutant Release Inventory, vol. 139, no. 8 (Canadian Environmental Protection Act, 1999).
- Chapel, D.G., Mariz, C.L., 1999. Recovery of CO₂ from flue gases: commercial and trends. In: *Originally Presented at the Canadian Society of Chemical Engineers Annual Meeting*.
- Craig, L.H., McLaughlin, B.D. Corrosive amine characterization. *Corrosion/96* (paper no. 394). NACE International, Houston.
- Crognale, G., 1999. *Environmental Management Strategies: The 21st Century Perspective*. Environmental Management & Engineering Series, vol. 5. Prentice Hall PTR, New Jersey.
- Cullinane, J.T., Rochelle, G.T., 2004. Carbon dioxide absorption with aqueous potassium carbonate promoted by piperazine. *Chem. Eng. Sci.* 59, 3619–3630.
- Davison, J., Freund, P., Smith, A., 2001. Putting Carbon Back into the Ground. IEA Greenhouse Gas R&D Programme.
- Dawodu, O.F., Meisen, A., 1994. Mechanism and kinetics of COS-induced diethanolamine degradation. *Ind. Eng. Chem. Res.* 33, 480–487.
- Dow Chemical Company, 1962. *Gas Conditioning Fact Book*, Dow Chemical Company, Michigan.
- DuPart, M.S., Bacon, T.R., Edwards, D.J., 1993. Understanding corrosion in alkanolamine gas treating plants. Part 2: Case histories show actual plant problems and their solutions. *Hydrocarbon Process.* 75–80.
- Energy Information Administration, 2003. *International Energy Annual 2003*. U.S. Department of Energy.
- Energy Information Administration, 2004. *Annual coal report 2004*. U.S. Department of Energy. DOE/EIA-0584(2004).
- Energy Information Administration, 2005. *International energy outlook 2005*. DOE/EIA-0484(2005).
- Energy Information Administration, 2006. *International energy outlook 2006*. U.S. Department of Energy. DOE/EIA-0484(2006).
- U.S. Environmental Protection Agency, 1995. AP 42: *Compilation of Air Pollutant Emission Factors*, Vol. 1: Stationary Point and Area Sources, 1995 (Chapter 1: External Combustion Source).
- European Sealing Association (ESA), 2005. *Sealing technology—BAT guidance notes*. ESA Publication No. 014/05.
- Fan, D., Kolp, L., Huett, D.S., Sargent, M.A., 2000. Role of impurities and H₂S in refinery lean DEA system corrosion. *Corrosion/2000* (paper no. 494). NACE International, Houston.
- The Great Lakes Binational Toxics Strategy, 1997. *The Canada-United States strategy for the virtual elimination of persistent toxic substances in the Great Lakes basin*.
- Gupta, M., Coyle, I., Thambimuthu, K., 2003. CO₂ capture technologies and opportunities in Canada. In: *Canadian CC&S Technology Roadmap Workshop*.
- Haslegrave, J.A., Hedges, W.M., Montgomerie, H.T.R., O'Brien, T.M., 1992. The development of corrosion inhibitors with low-environmental toxicity. In: *Proceedings of 67th SPE Conference*. (paper no. SPE 24846).
- Huang, H., Chang, S.-G., Dorchak, T., 2002. Method to regenerate ammonia for the capture of carbon dioxide. *Energy Fuels* 16, 904–910.
- Jamal, A., Meisen, A., 2001. Kinetics of CO induced degradation of aqueous diethanolamine. *Chem. Eng. Sci.* 56, 6743–6760.
- Kohl, A.L., Nielsen, R., 1997. *Gas Purification*, fifth ed. Gulf Publishing Company, Texas.
- Litchewski, M.J., 1996. More experiences with corrosion and fouling in refinery amine systems. *Corrosion/96* (paper no. 391). NACE International, Houston.
- Liu, H.J., Dean, J.W., 1995. Neutralization technology to reduce corrosion from heat-stable amine salts. *Corrosion/95* (paper no. 572). NACE International, Houston.
- Mago, B.F., West, C.W., 1976. Corrosion inhibitors for alkanolamine gas treating system. U.S. Patent 3,959,170.
- Malcolm, L.K., Meisen, A., 1985. Mechanisms and kinetics of diethanolamine degradation. *Ind. Eng. Chem. Fundam.* 24, 129–140.
- McCullough, J.G., Nielsen, R.B., 1996. Contamination and purification of alkaline gas treating solutions. *Corrosion/96* (paper no. 396). NACE International, Houston.
- McMahon, A.J., Harrop, D., 1995. Green corrosion inhibitors: an oil company perspective. In: *Proceedings of Corrosion 95*. (paper no. 32).
- Mimura, T., Shimijo, S., Suda, T., Iijima, M., Mitsuoka, S., 1995. Research and development of energy saving technology for flue gas carbon dioxide recovery and steam system in power plant. *Energy Convers. Manag.* 36, 397–400.
- Nielsen, R.B., Lewis, K.R., 1995. Corrosion in refinery amine system. *Corrosion/95*, NACE, Houston (paper no. 571).
- Ohta, K., 1982. Method of defoaming amine solutions. U.S. Patent 4,313,917.
- Occupational Safety & Health Administration (OSHA). Occupational safety and health standards (29CFR1910, subpart Z).
- Pauley, C.R., 1991. Face the facts about amine foaming. *Chem. Eng. Prog.* 33–38.
- Perry, R.H., Green, D.W., Maloney, J.O., 1997. *Perry's Chemical Engineers' Handbook*, seventh ed. The McGraw-Hill Companies Inc..
- Pohorecki, R., Kucharski, E., 1991. Desorption with chemical reaction in the system CO₂-aqueous solution of potassium carbonate. *Chem. Eng. J. (Amsterdam, Netherlands)* 46, 1–7.
- Resource Conservation and Recovery Act (RCRA). Identification and listing of hazardous waste (40CFR261, subpart D).
- Rooney, P.C., DuPart, M.S., 2000. Corrosion in alkanolamine plants: causes and minimization. *Corrosion/2000* (paper no. 494). NACE International, Houston.

- Rooney, P.C., Bacon, T.R., DuPart, M.S., 1997. Effect of heat stable salts on solution corrosivity of MDEA-based Alkanolamine plants. Part III. In: Proceedings of 47nd Annual Laurance Reid Gas Conditioning Conference, The University of Oklahoma, Norman, Oklahoma, pp. 12–30.
- Savage, D.W., Astarita, G., Joshi, S., 1980. Chemical absorption and desorption of carbon dioxide from hot carbonate solutions. *Chem. Eng. Sci.* 35, 1513–1522.
- Schnell, J., Barwick, K., Shah, A., 2004. Hazardous Waste Source Reduction Assessment of Selected Sectors of California Chemical Industry. California Environmental Protection Agency.
- Singh, W.P., Bockris, J.O'M., 1996. Toxicity issues of organic corrosion inhibitors: applications of QSAR model. In: Proceedings of Corrosion 96. (paper no. 225).
- Strazisar, B.R., Anderson, R.R., White, C.M., 2003. Degradation pathways for monoethanolamine in a CO₂ capture facility. *Energy Fuels* 17, 1034–1039.
- Tanthapanichakoon, W., Veawab, A., McGarvey, B., 2006. Electrochemical investigation on the effect of heat-stable salts on corrosion in CO₂ capture plants using aqueous solution of MEA. *Ind. Eng. Chem. Res.* 45, 2586–2593 (special issue on CO₂ Capture).
- Toronto Municipal Code, 2003. Article I: sewage and land drainage (Chapter 681).
- Tseng, P.C., Ho, W.S., Savage, D.W., 1988. Carbon dioxide absorption into promoted carbonate solutions. *AIChE J.* 34, 922–931.
- The Government of Canada and Ontario, 2002. Canada-Ontario agreement respecting the Great Lakes basin ecosystem.
- Veawab, A., 2000. Corrosion and corrosion control in CO₂ absorption process using aqueous amine solutions. Ph.D. Thesis. University of Regina.
- Veldman, R., 1989. How to reduce amine losses. In: Paper Presented at Petroenergy. pp. 23–27.
- Veldman, R.R., Trahan, D.O., 1997. Oxygen scavenging solutions for reducing corrosion by heat stable amine salts. U.S. Patent 5,686,016.
- Veldman, R.R., Trahan, D.O., 2001. Gas treating solution corrosion inhibitor. U.S. Patent 6,299,836.